

Resonantly Amplified Vibronic Symmetry Breaking

G.J. Rathbone,¹ E.D. Poliakoff,¹ J.D. Bozek,² and R.R. Lucchese³

¹Department of Chemistry, Louisiana State University, Baton Rouge, Louisiana 70803,

²Lawrence Berkeley National Laboratory, University Of California, Berkeley California, 94720

³Department of Chemistry, Texas A&M University, College Station, Texas, 77843

INTRODUCTION

When a molecule is photoionized, the photoelectron traverses the molecular environment as it exits. Because the photoelectron senses a highly anisotropic potential during its escape [1,2], surprising and useful phenomena (e.g., XANES) arise naturally [3,4]. In this vein, we have uncovered an unexpected and novel photoionization phenomenon, *resonantly amplified vibronic symmetry* breaking. It is normally assumed that (single quantum) excitation of non-totally symmetric vibrational modes is forbidden, owing to fundamental symmetry constraints. The results reported here demonstrate that this selection rule can be violated, owing to coupling between the photoelectron and the vibrational angular momentum associated with the degenerate bending vibration. Moreover, the magnitude of the effect is large, resulting in excitation of nominally forbidden modes with as much intensity as is observed for allowed vibrational modes. Vibrationally resolved spectra were taken the Advanced Light Source, and we generated energy-dependent photoelectron spectra for $4\sigma_g^{-1}$ photoionization of CO_2 . This work demonstrates that there can be strong correlation between electronic and nuclear degrees of freedom during photoionization. It also lends new insight into molecular spectroscopy, and has potential for important applications in a variety of areas by illuminating new connections between ionization dynamics and nuclear motion.

EXPERIMENT

Photoelectron spectra are acquired at the magic angle over a broad range of incident photon energies. The apparatus for acquiring gas-phase photoelectron spectra is described in detail elsewhere [5]. Briefly, the experiment was done at beamline 10.0.1 – an undulator beamline equipped with a spherical grating monochromator (SGM). These measurements used the 380 line/mm grating for $20 \leq h\nu_{\text{exc}} \leq 50$ eV and 925 line/mm grating for $50 \leq h\nu_{\text{exc}} \leq 110$ eV. The excitation bandwidth was held constant at 10 meV, and the ability to work at this comparatively high resolution over a very broad energy range was a critical aspect of the current study. The photoelectrons were analyzed with a Scienta hemispherical electron energy analyzer (model SES-200), and this analyzer is well-suited for generating high resolution photoelectron spectra. The pass energy of the analyzer was 2 eV, and slit widths of 0.04 cm, 0.05 cm, and 0.06 cm were used, corresponding to analyzer resolutions of 2 meV, 2.5 meV, 3 meV, respectively. At $h\nu_{\text{exc}} = 25$ eV, the overall resolution of the photoelectron spectrum was 12 meV, which is consistent with the photon and photoelectron bandwidths.

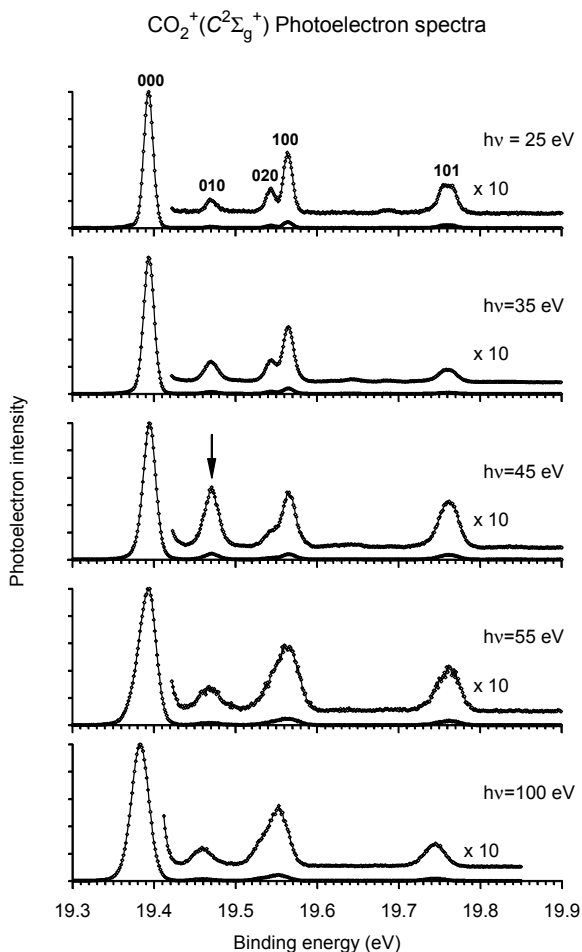


Figure 1. This figure shows magic angle photoelectron spectra for $4\sigma_g^{-1}$ photoionization of CO_2 at selected photon energies. The labels of the vibrational assignments are given in the top frame. The peak labeled 010 corresponds to the ion with one quantum of bending excitation. Note that both the $v^+= (010)$ and $v^+= (101)$ levels are symmetry forbidden. Moreover, both of these forbidden features display strongly energy dependent behavior. In particular, note how intense the (010) peak is at $h\nu = 45$ eV.

RESULTS AND DISCUSSION

Selected photoelectron spectra are shown in Fig. 1. The vibrational assignments are shown in the top frame. These spectra indicate that it is possible to resolve low frequency vibrational modes in polyatomic photoionization over a broad range of energies. This has not been accomplished previously with photoelectron spectroscopy. Spectra such as those shown in Fig. 1 can be used to map out the energy dependence of the vibrational branching ratios for the bending degree of freedom. Specifically, one can take the ratio of the (010) peak (i.e., the nominally forbidden transition corresponding to excitation of one quantum of bending) to that of the main peak (the 000 level). This was done and the results are shown in Fig. 2.

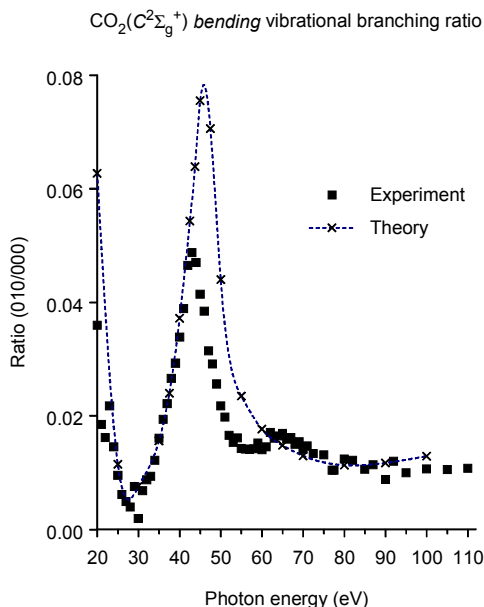


Figure 2. Vibrational branching ratio for bending excitation. The strong resonant enhancement of the nominally forbidden transition is apparent from the peak in the branching ratio at $h\nu \approx 42$ eV.

The branching ratio displays a strong enhancement at $h\nu = 42$ eV, which is the position of a continuum resonance in the $4\sigma_g \rightarrow k\sigma_u$ channel [6]. The data show that the breakdown in the selection rule is *strongly amplified by the presence of the continuum resonance*. In addition to the experimental data, Fig. 2 also shows results from calculations employing Schwinger variational wavefunctions for the continuum electron. The theoretical model used to generate the curve in Fig. 2 does not include any interchannel coupling effects, demonstrating that the resonance in the continuum channel is *directly amplifying the intrachannel effects* that result in a breakdown of the selection rule [7]. These results shown here for bending motion indicate that it is possible and desirable to probe connections between photoionization dynamics and more complex nuclear motions than have been studied previously.

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Principal investigator: Erwin Poliakoff, Department of Chemistry, Louisiana State University, Baton Rouge, LA 70808. Email: erwin.poliakoff@chem.lsu.edu. Telephone: 225-578-2933.